



# Heterogeneous distributions of reactive transport properties

$k$  &  $K_d$  ?

## A Geologic Framework for Reactive Solute Transport Properties in Sedimentary Aquifers

DOE-ERSP Annual PI Meeting, April 7, '08

$k$  &  $K_d$  ?

Reactivity,  $K_d$ ,  $kr$ , etc.

**Richelle M Allen-King  
University at Buffalo (SUNY)**

Permeability,  $k$

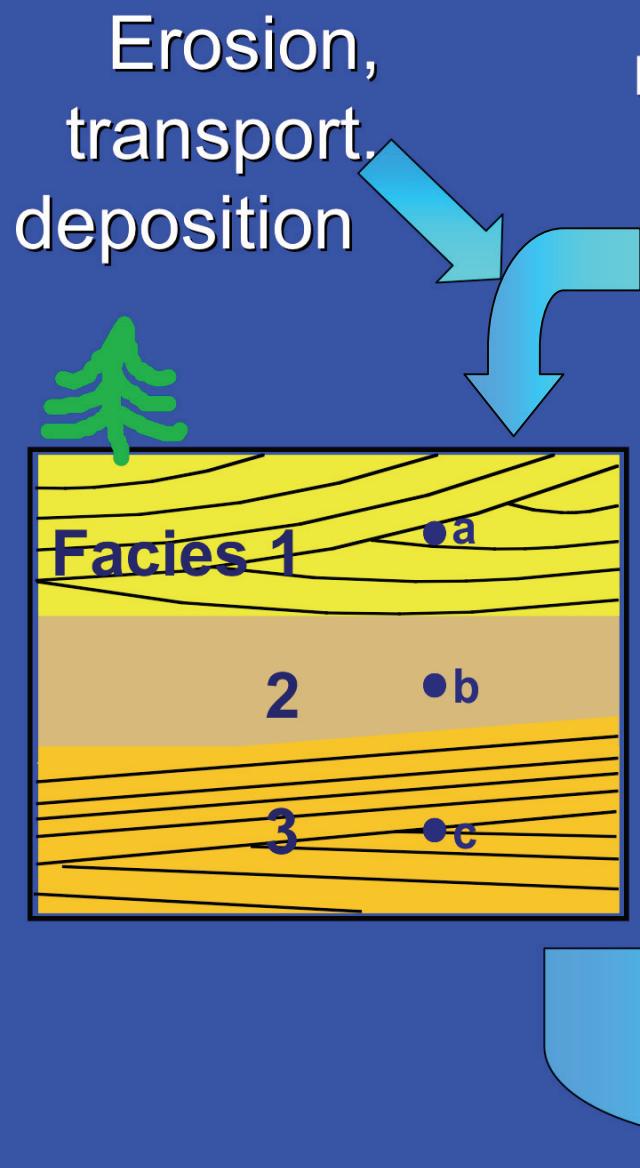
# **Surficial geology of the US is...**

**in direct contact with anthropogenic  
pollutant sources**

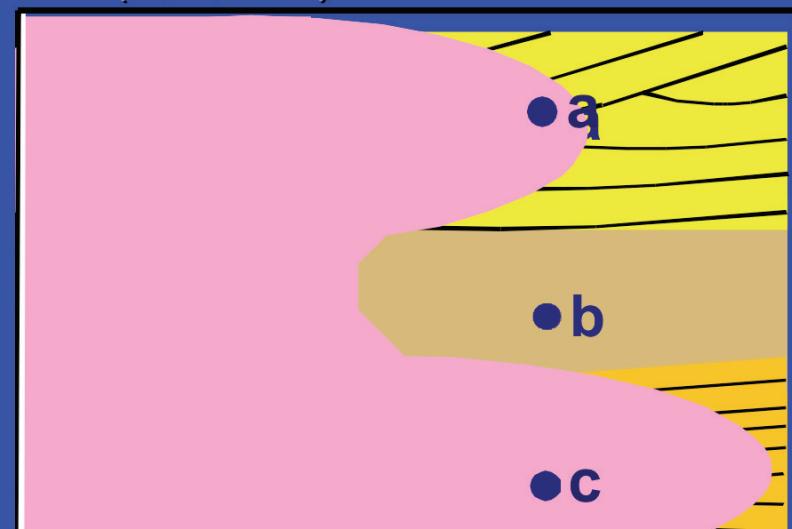
**sediments are blues,  
greens, oranges, yellows  
residual materials  
developed on sedimentary  
rocks are purples)**

*Surficial geology of US (Soller, 1990 & Reheis  
compilers, USGS open file report 03-275)*

# Conceptual Model of Aquifer Heterogeneity



$$V_{(a,b,\text{or } c)} = f(K_i, Kd_i)$$

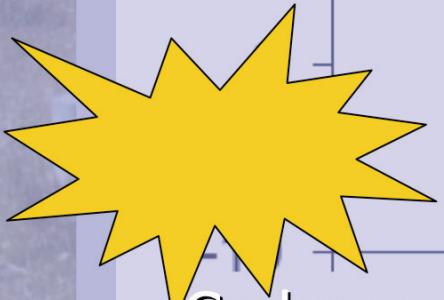


# Borden plumes

- ❑ Simple (e.g., young) reactions (sorption/desorption)
- ❑ Plumes (CT&PCE)  
~20-400 m<sup>3</sup> w/  
transport distances  
of meters to tens of  
m's

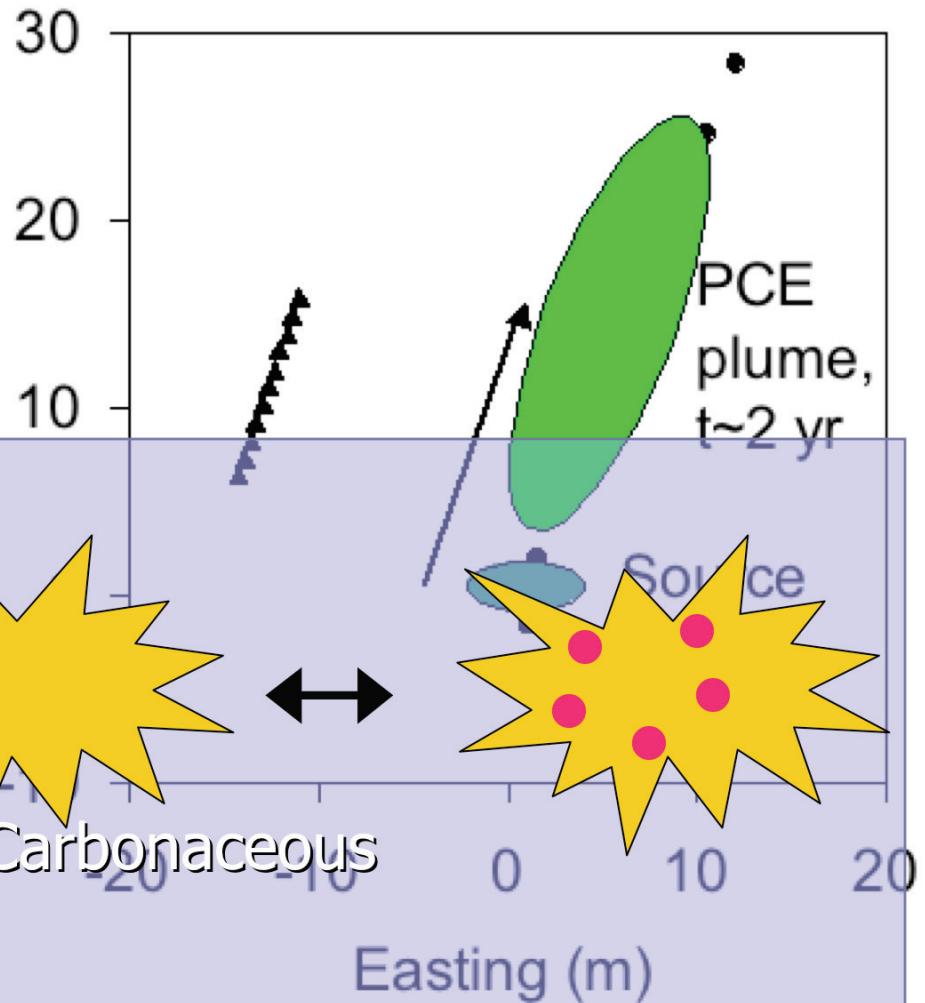
Organic  
Contaminant Matter

+

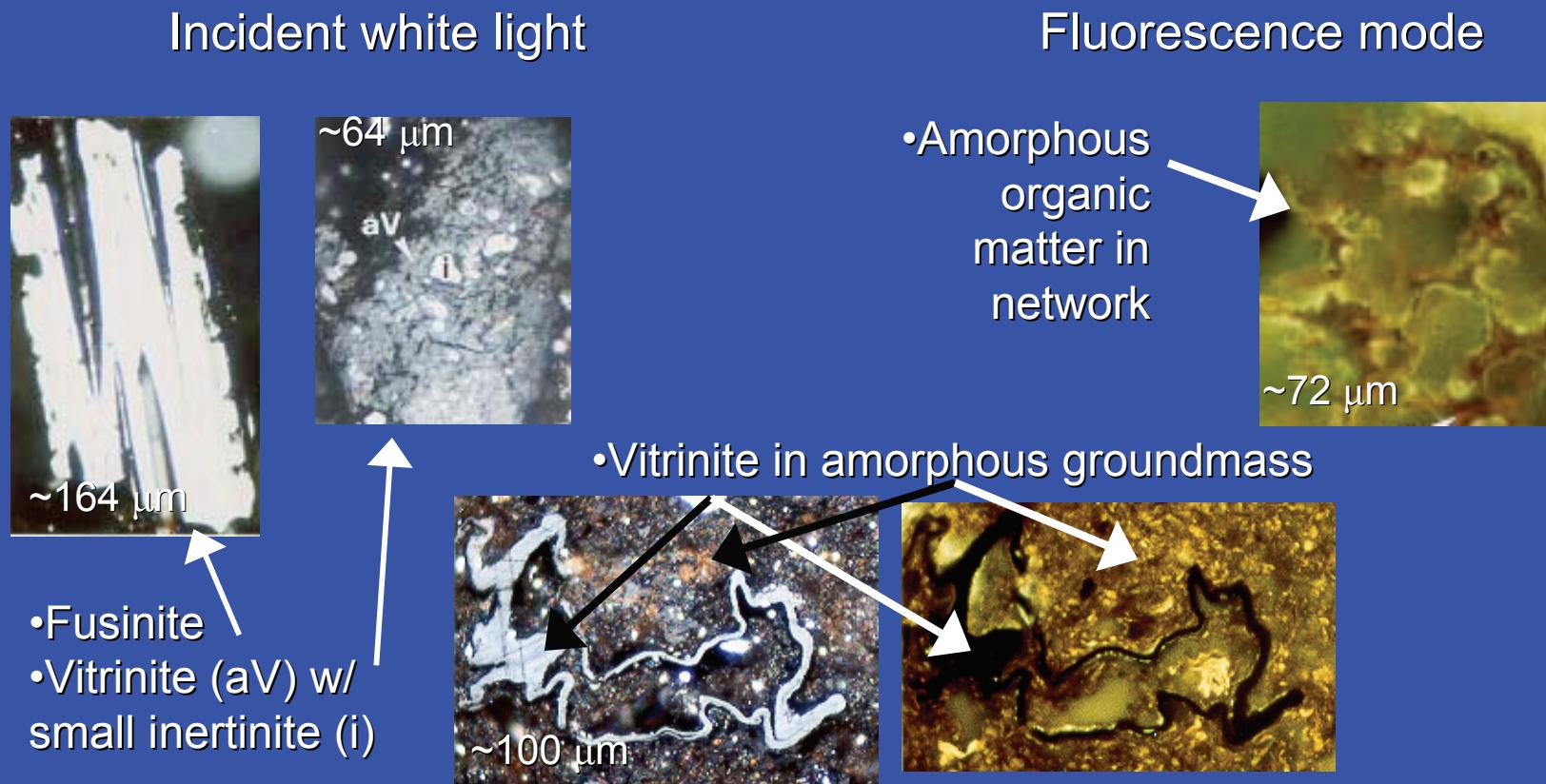


Carbonaceous

Easting (m)

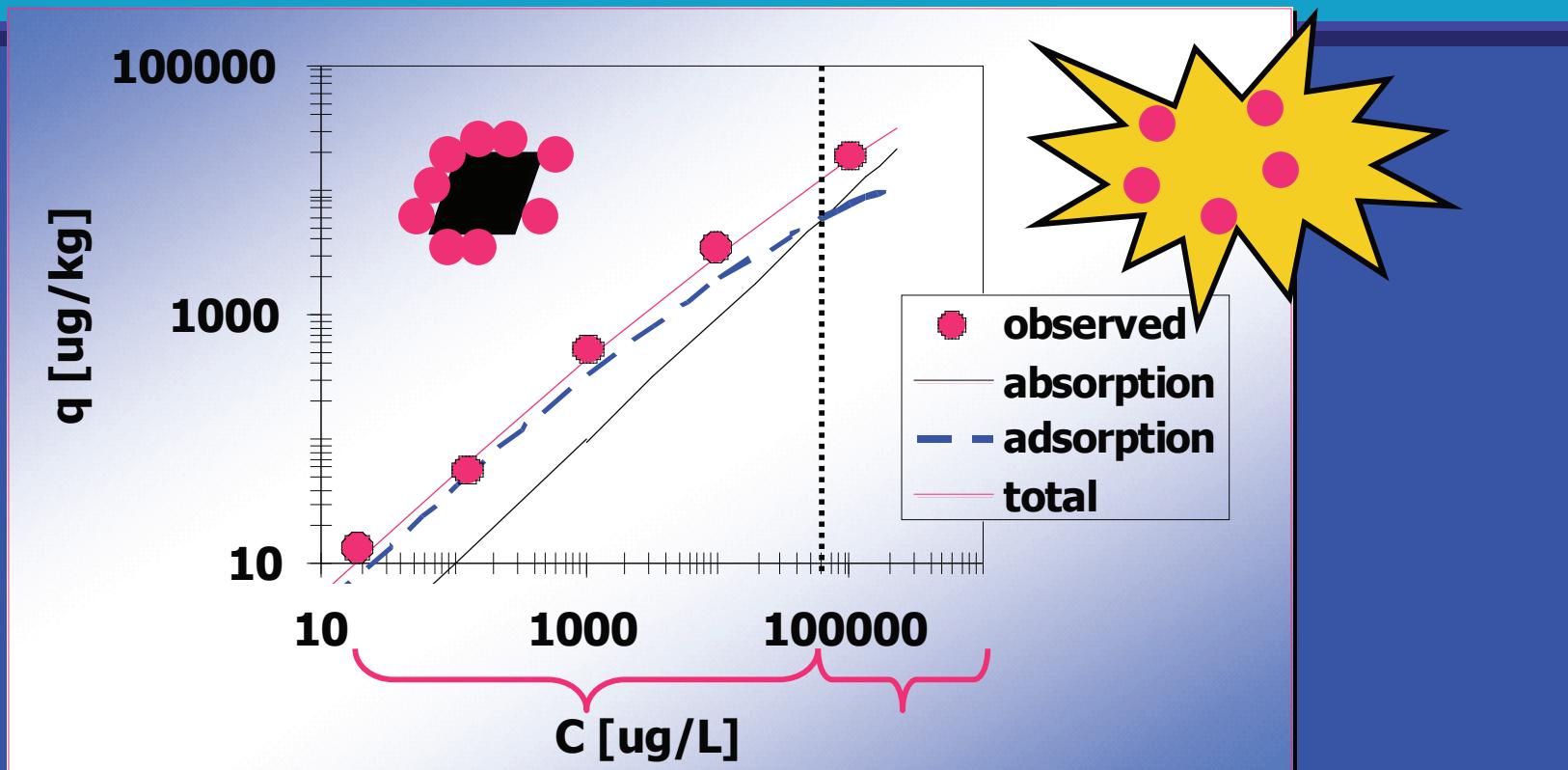


# Heterogeneous Borden carbonaceous matter



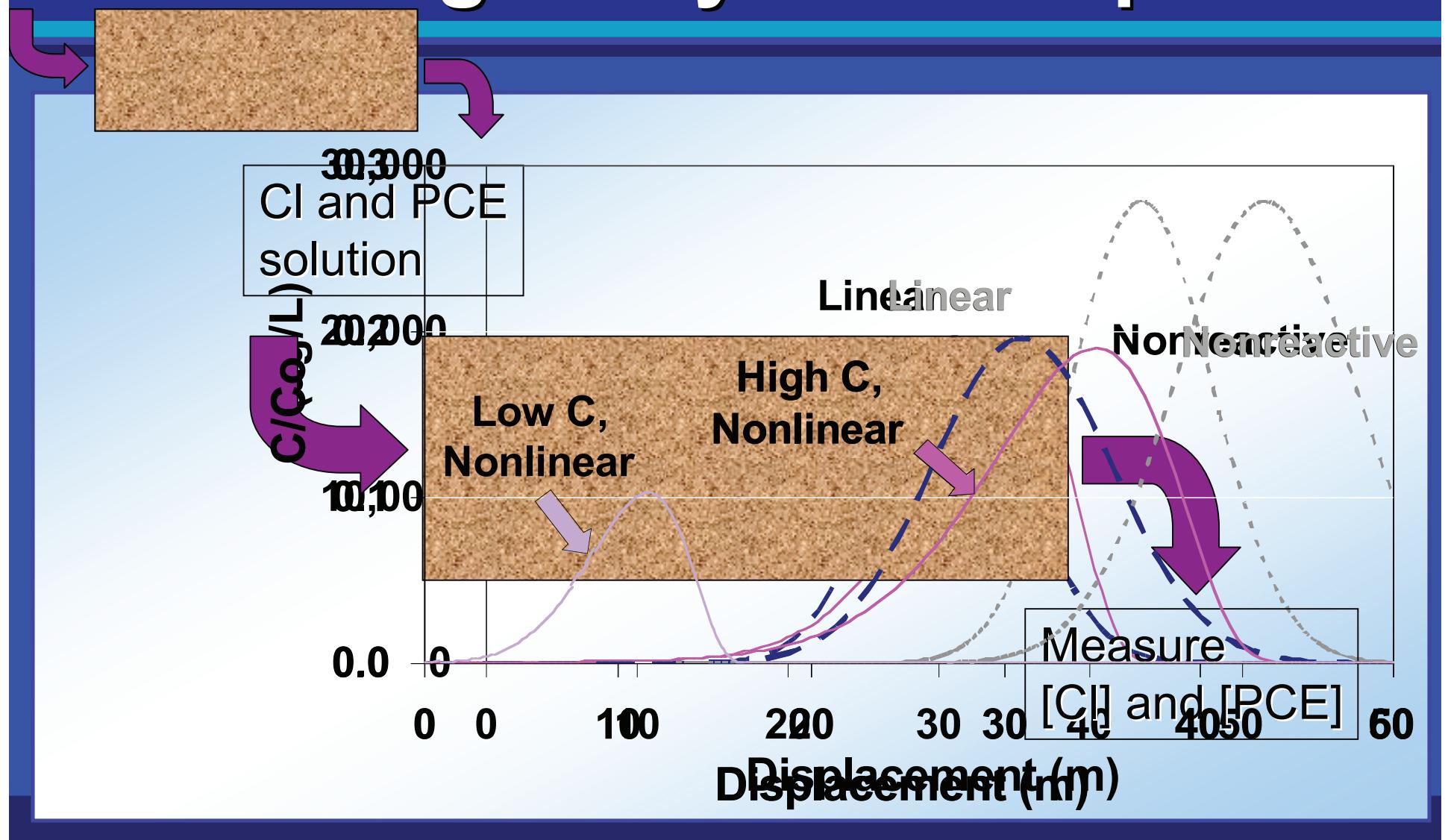
Petrography by Bertrand Louigi, University of Tübingen

# Adsorption dominates at low aqueous concentration

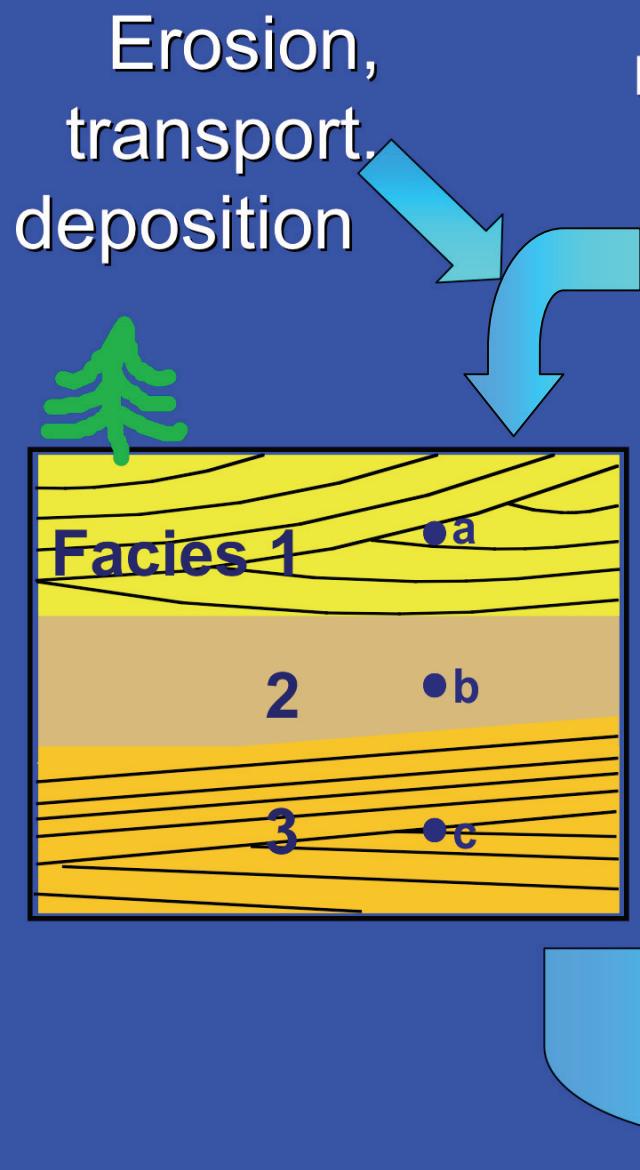


Absorption (the standard empirical approach) dominates at high relative concentrations,  $C > \sim 0.5\%$  solubility

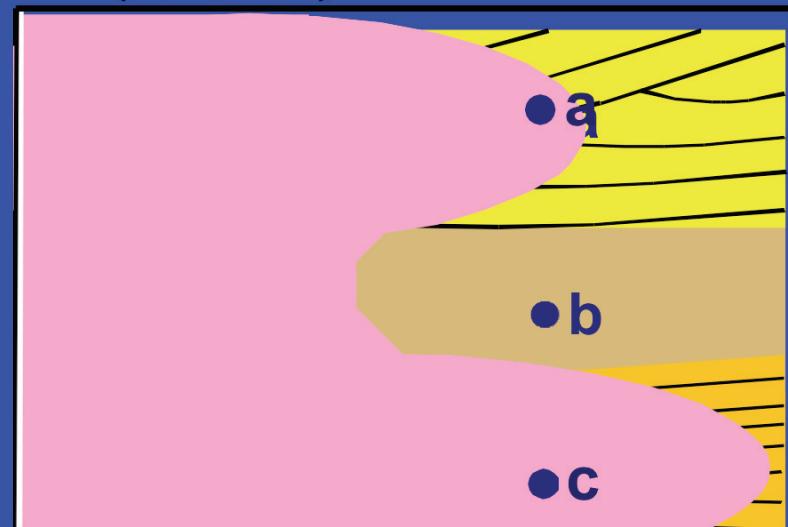
# Impact of grain-scale heterogeneity on transport



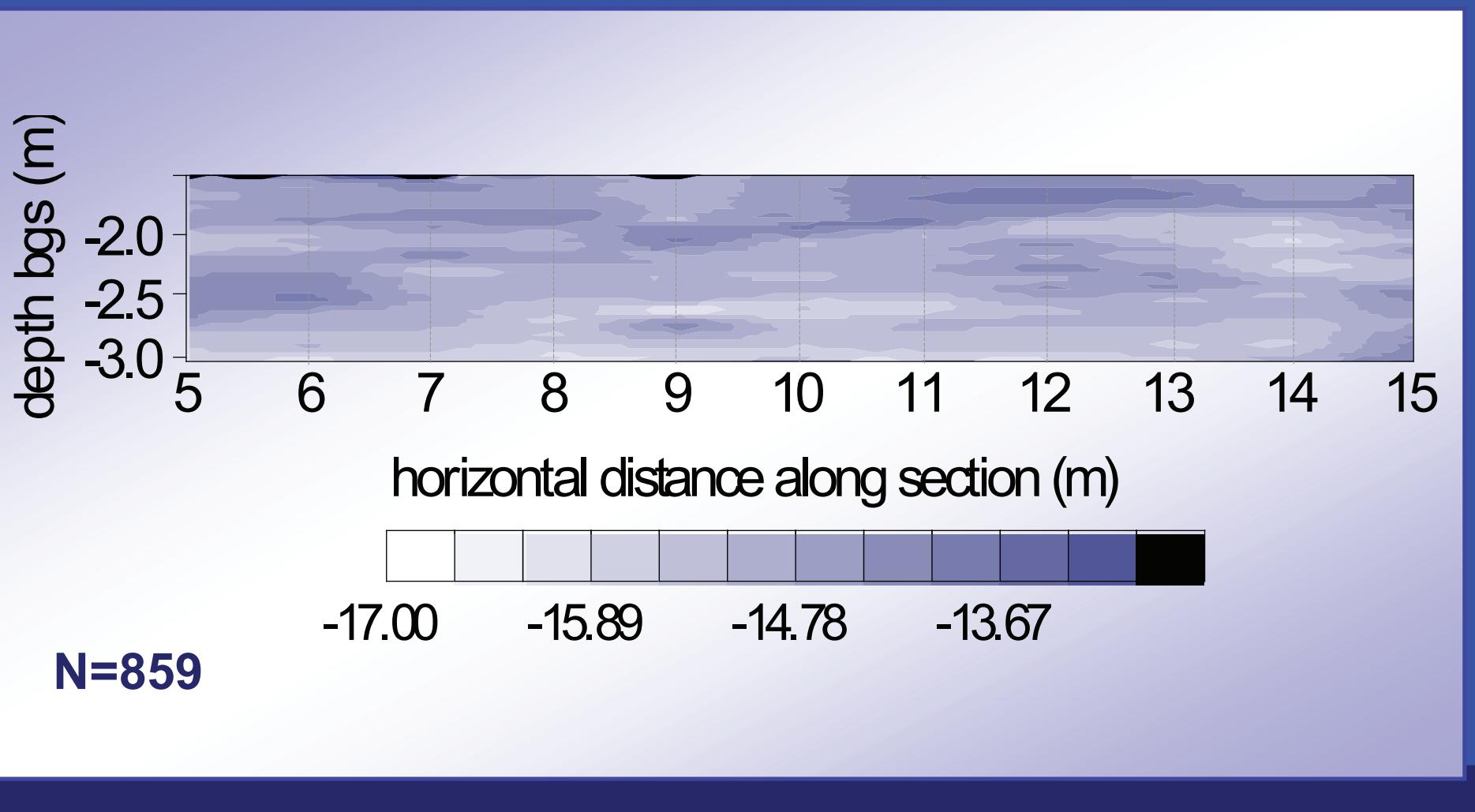
# Conceptual Model of Aquifer Heterogeneity



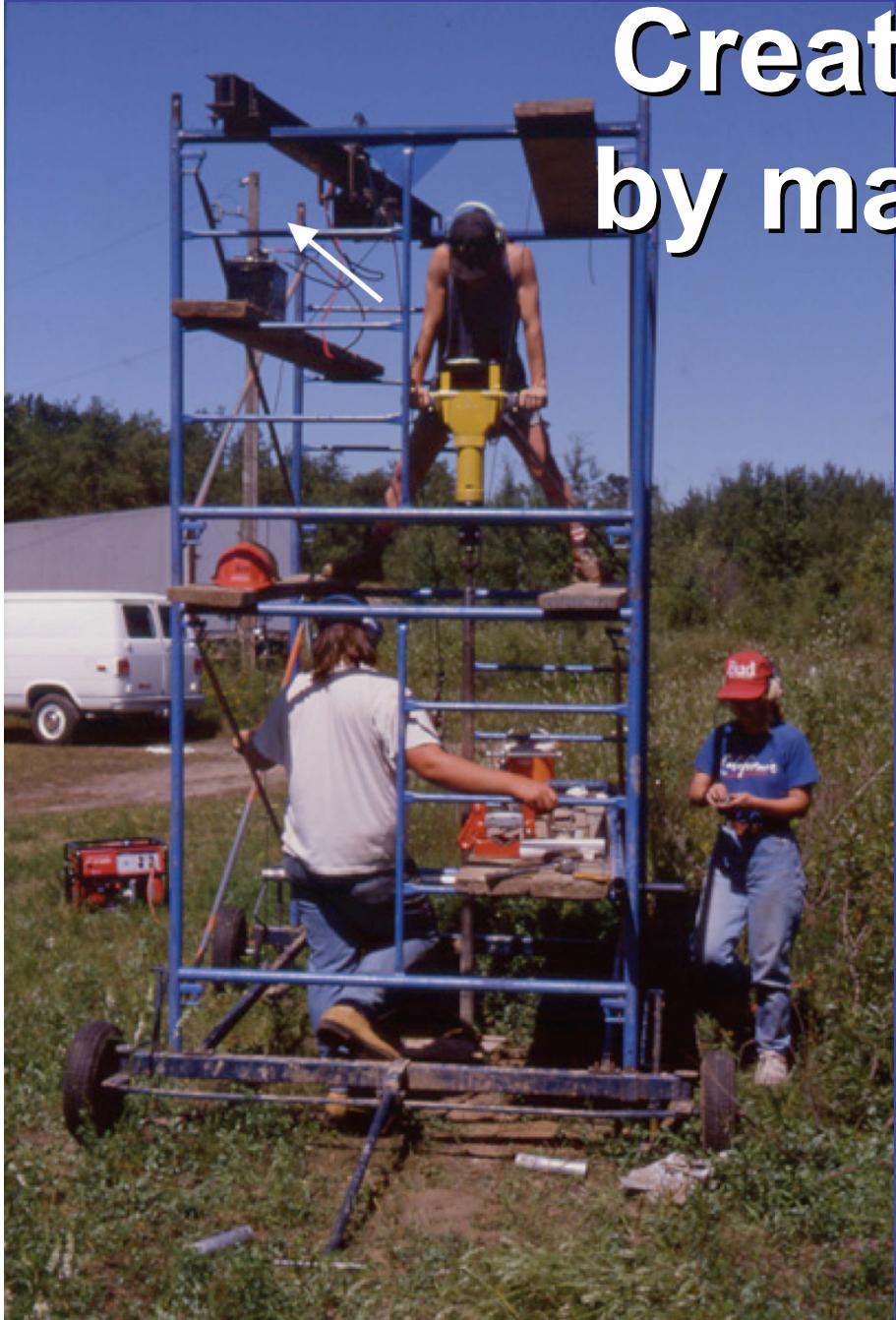
$$V_{(a,b,\text{or } c)} = f(K_i, Kd_i)$$



# Contour plot of ln-transformed permeability from 11 cores



# Create 'indicator' data by mapping lithofacies



MCG  
massive  
coarse grained

DPL  
distinct plane  
laminated

MFG  
massive  
fine grained

**Elevation (masl)**

220.0

219.5

219.0

218.5

218.0

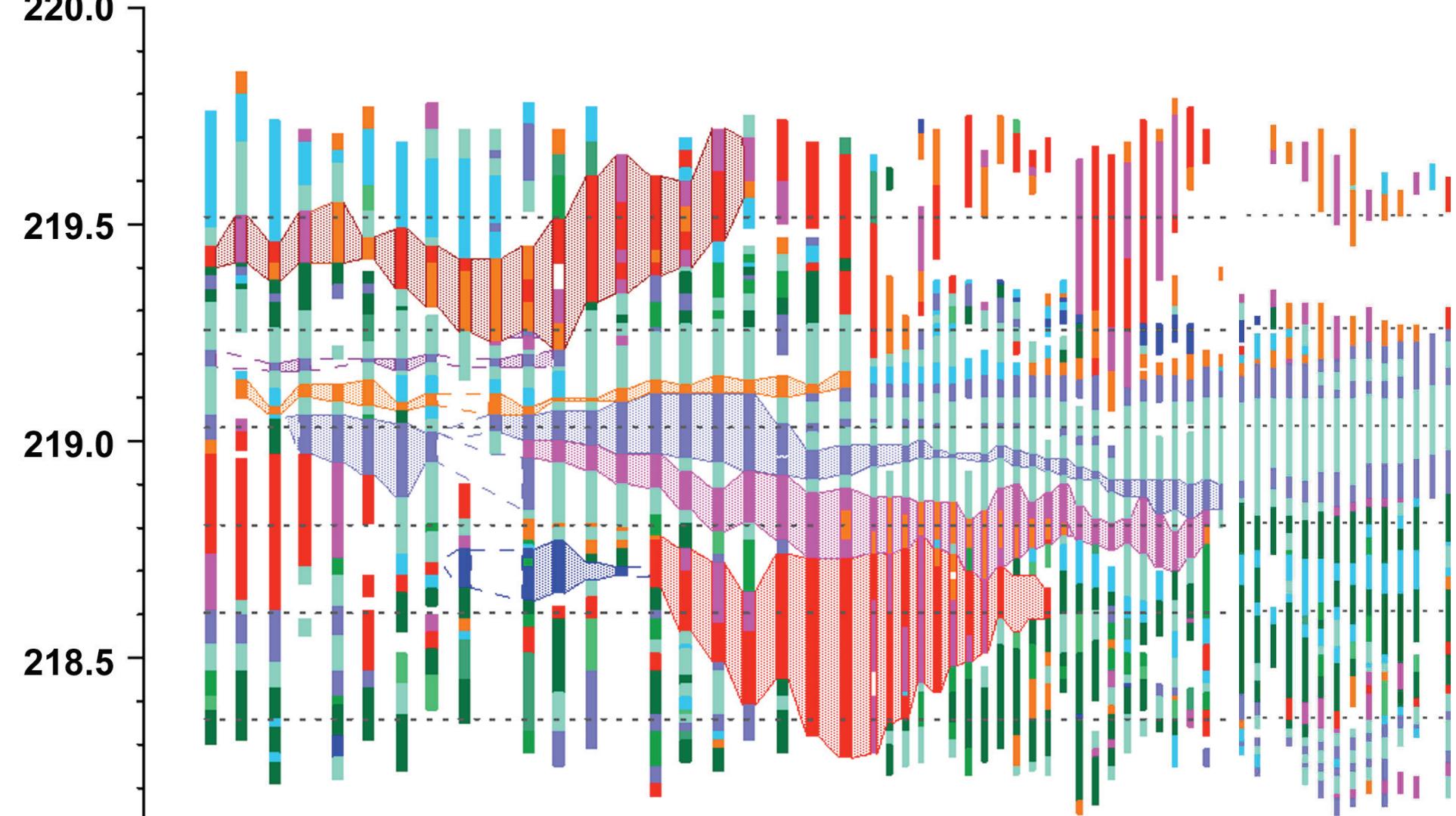
5

10

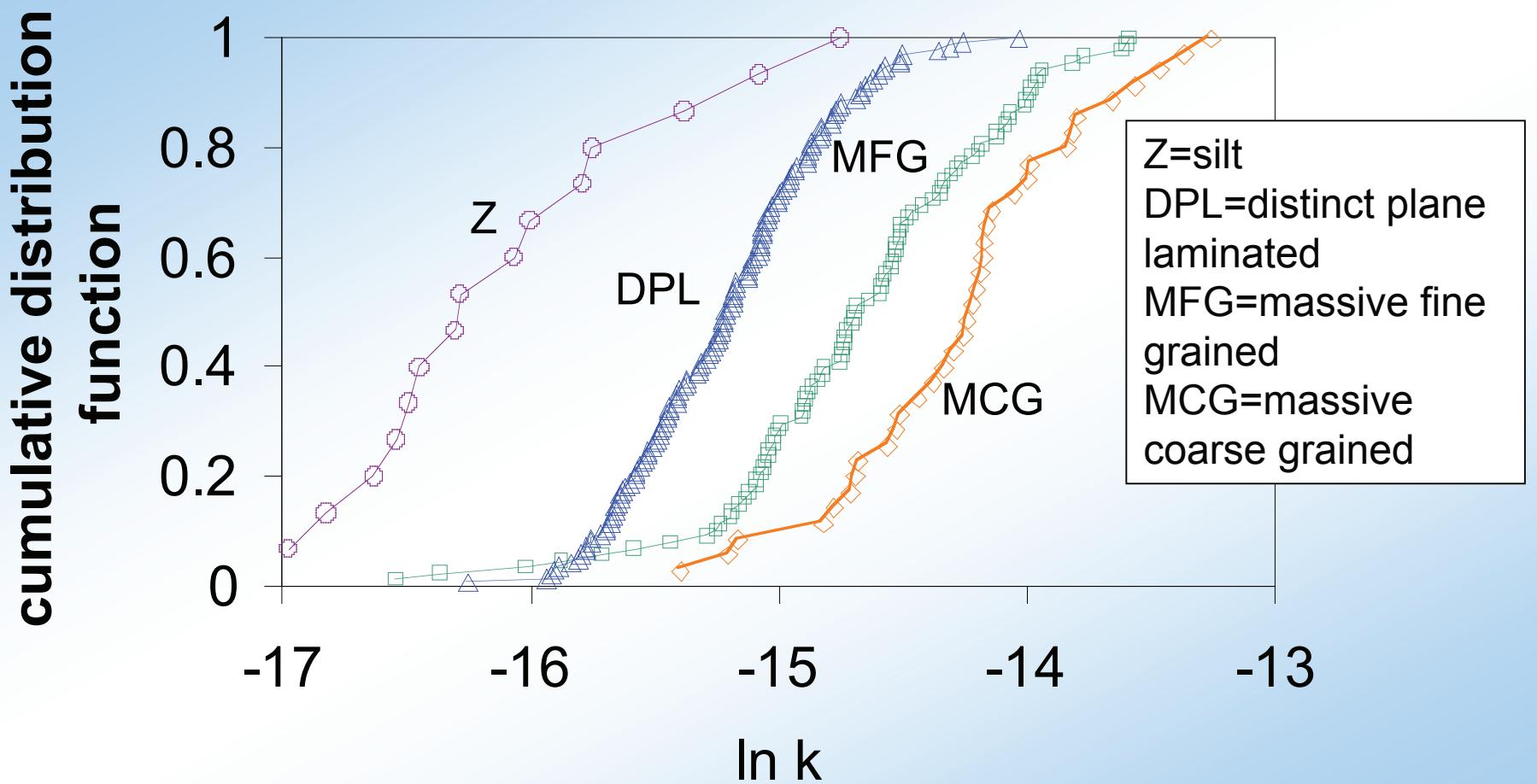
15

20

**Northing (m)**



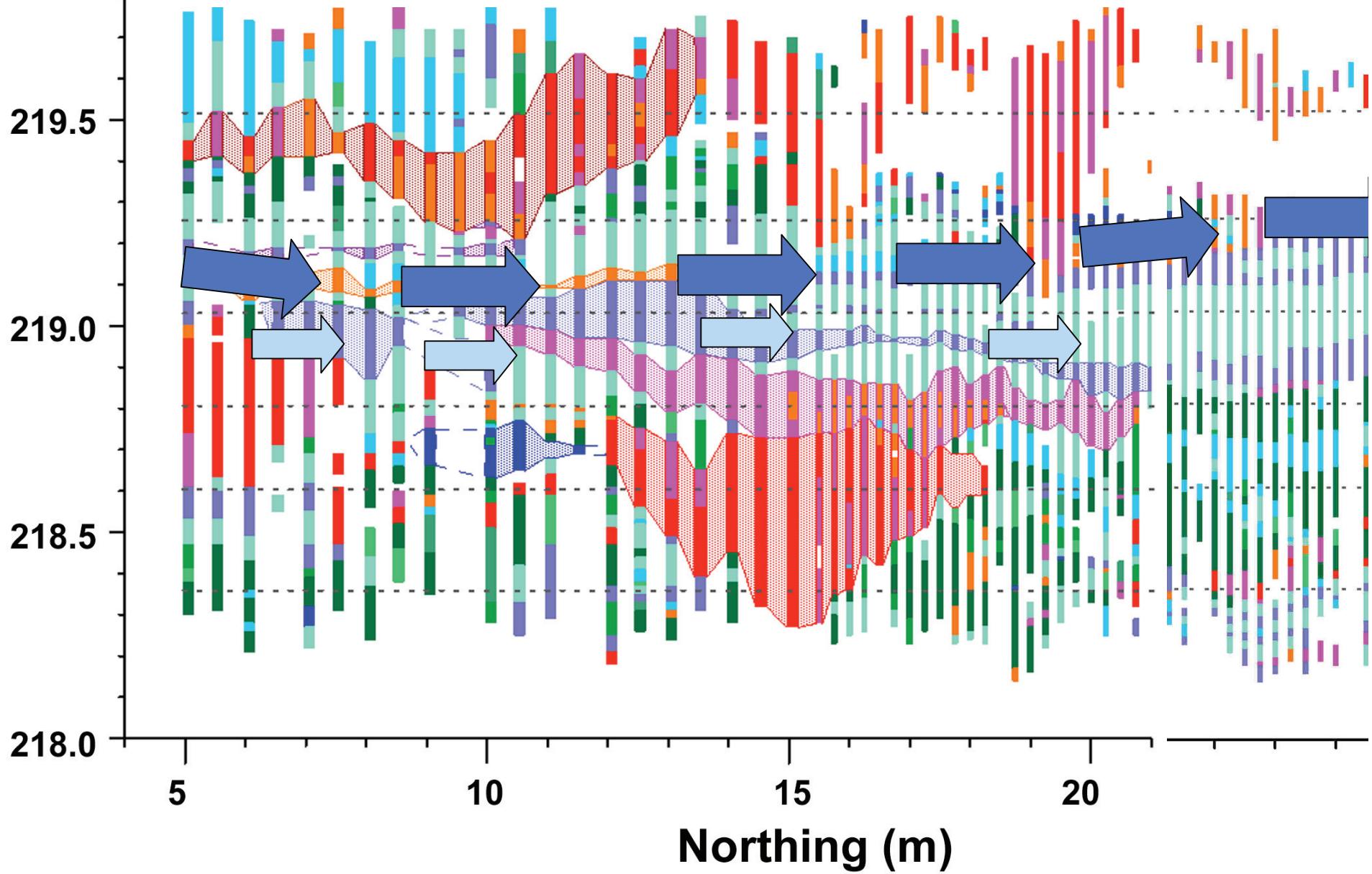
# Permeability ( $k$ ) distribution differs by lithofacies



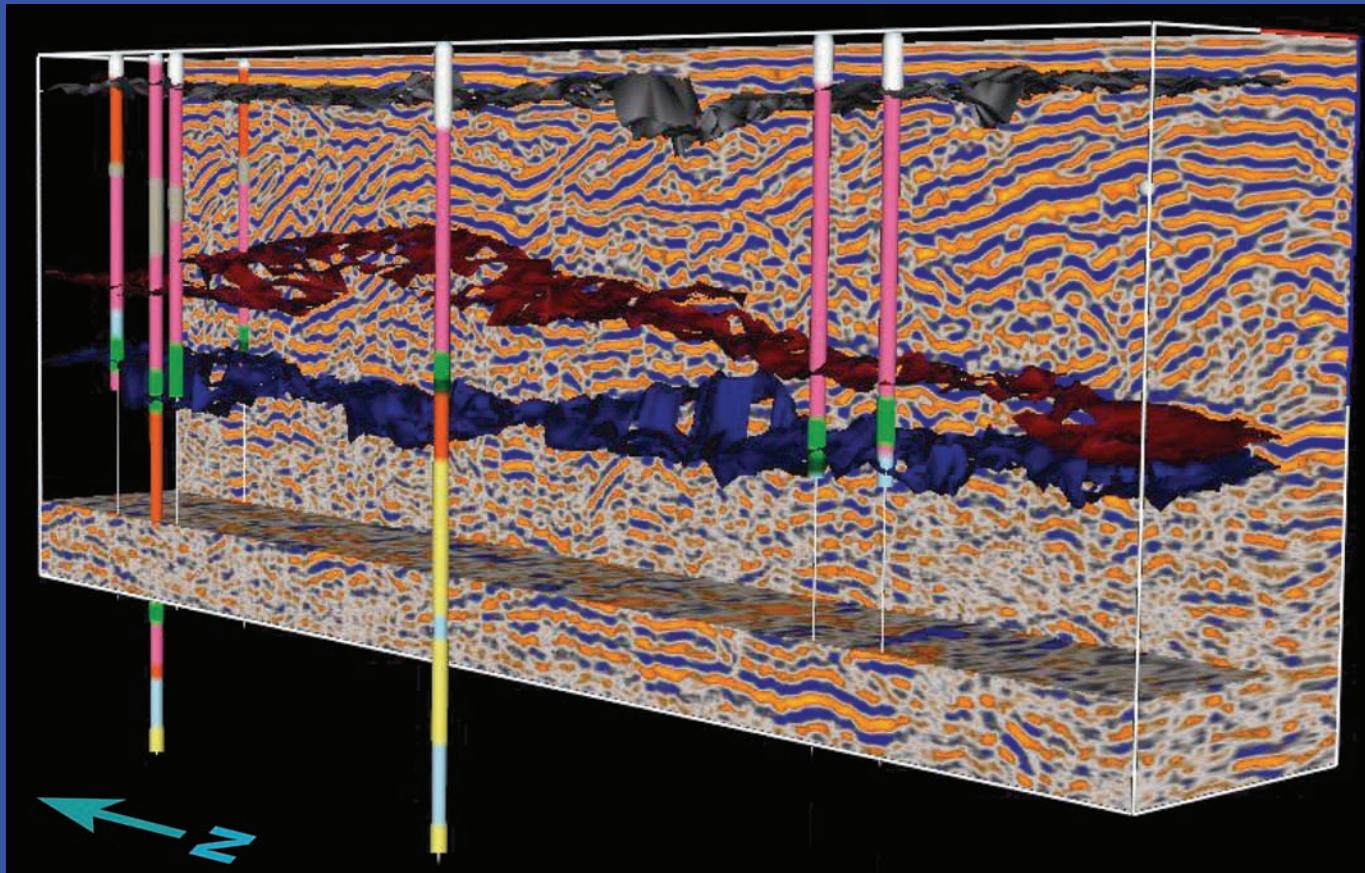
Elevation (masl)

220.0

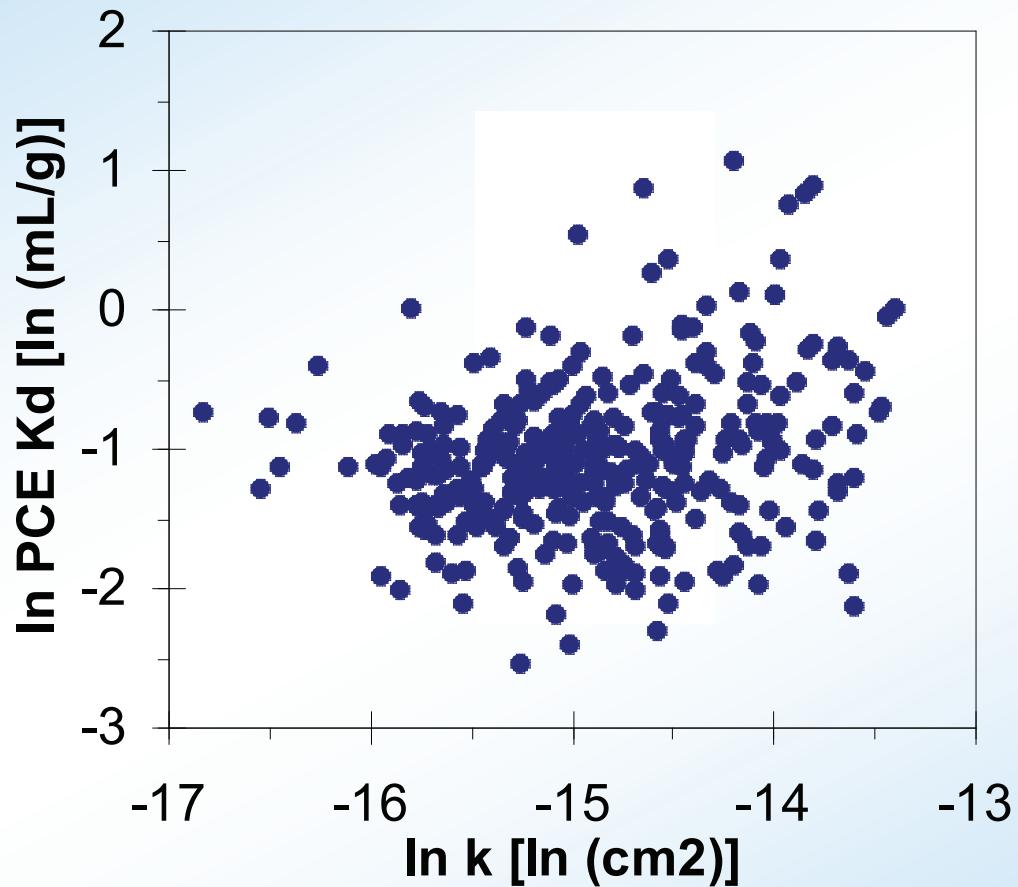
# Permeability contrasts focus flow



# Geophysical data provides facies classifications between cores

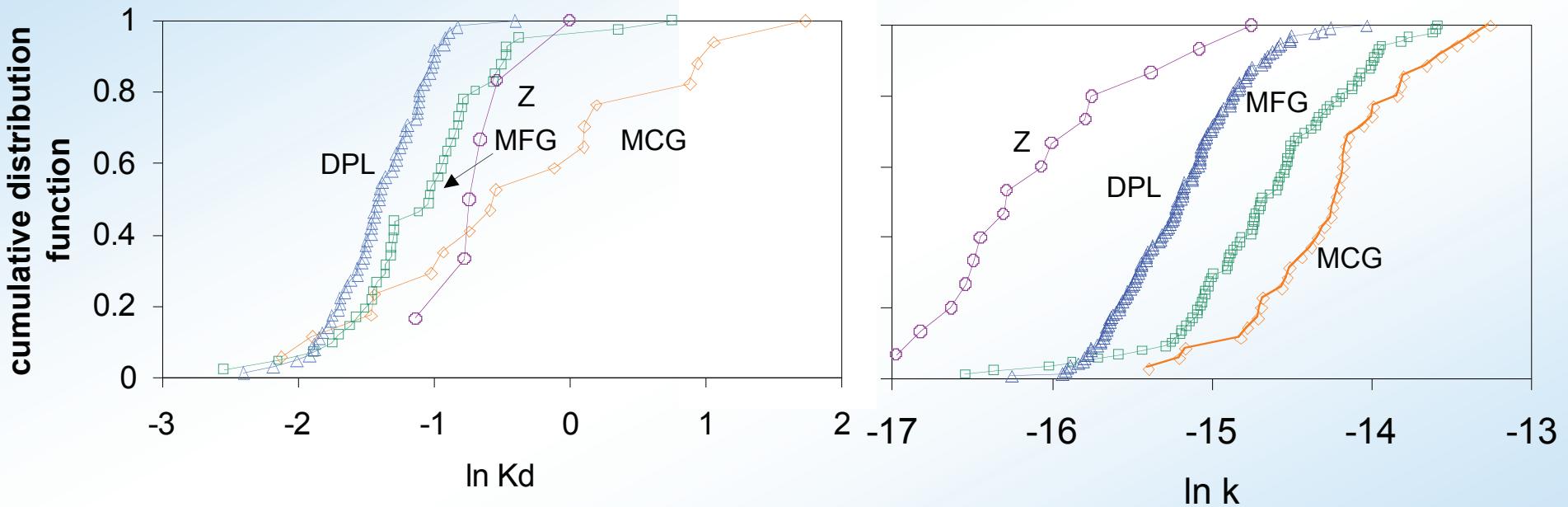


# Permeability-reactivity relation is not simple!



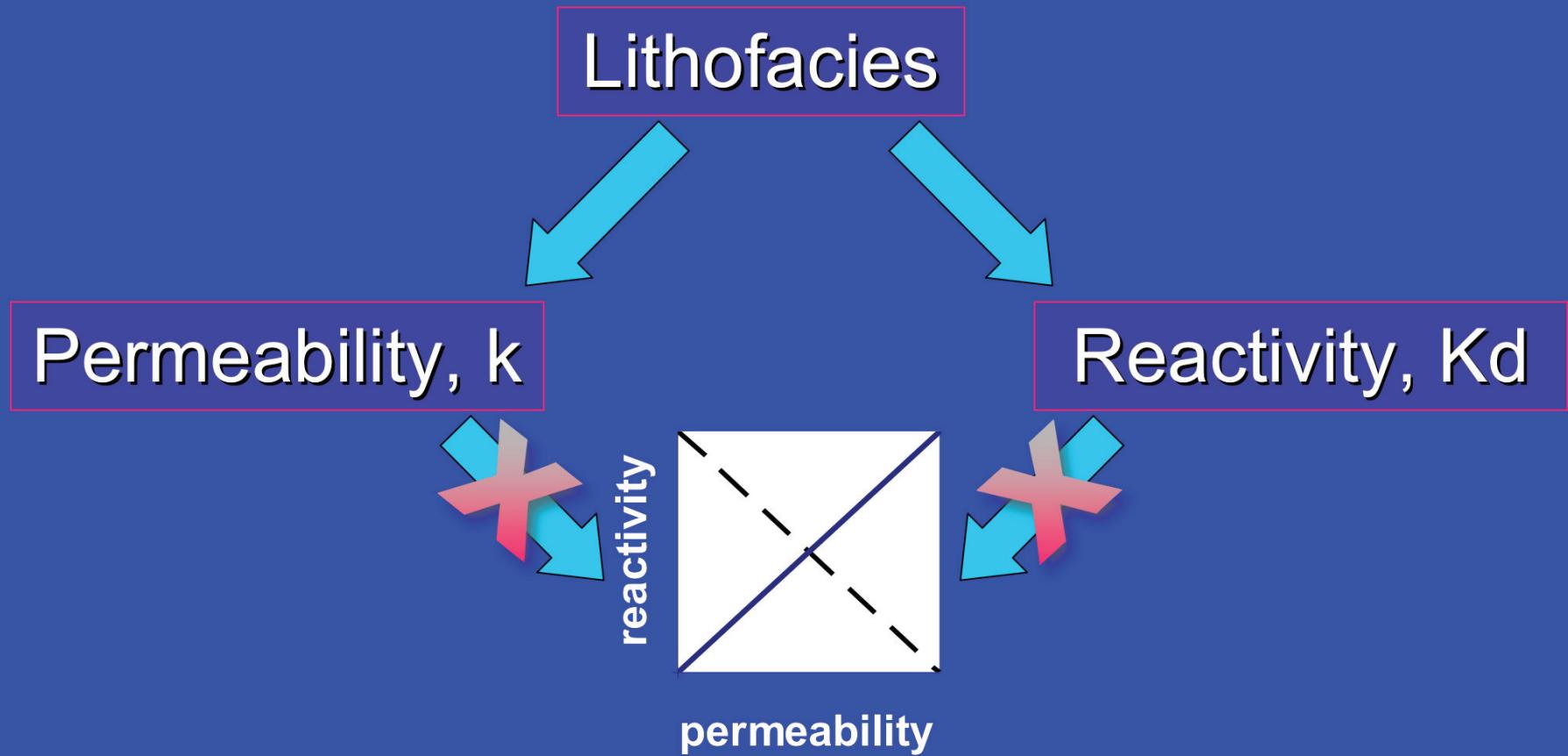
# Facies (or groups of facies) have distinct permeability & reactivity cdfs!

Different distribution patterns indicate that neither (+) or (-)  $k$ - $K_d$  correlation is appropriate (as commonly assumed)



Representative lithofacies samples from >90 cores and  
based on  $n_{K_d} > 500$ ;  $n_k > 1100$

# Reactivity and permeability are correlated to lithofacies



***Correlation is not simple***

**Elevation (masl)**

220.0

219.5

219.0

218.5

218.0

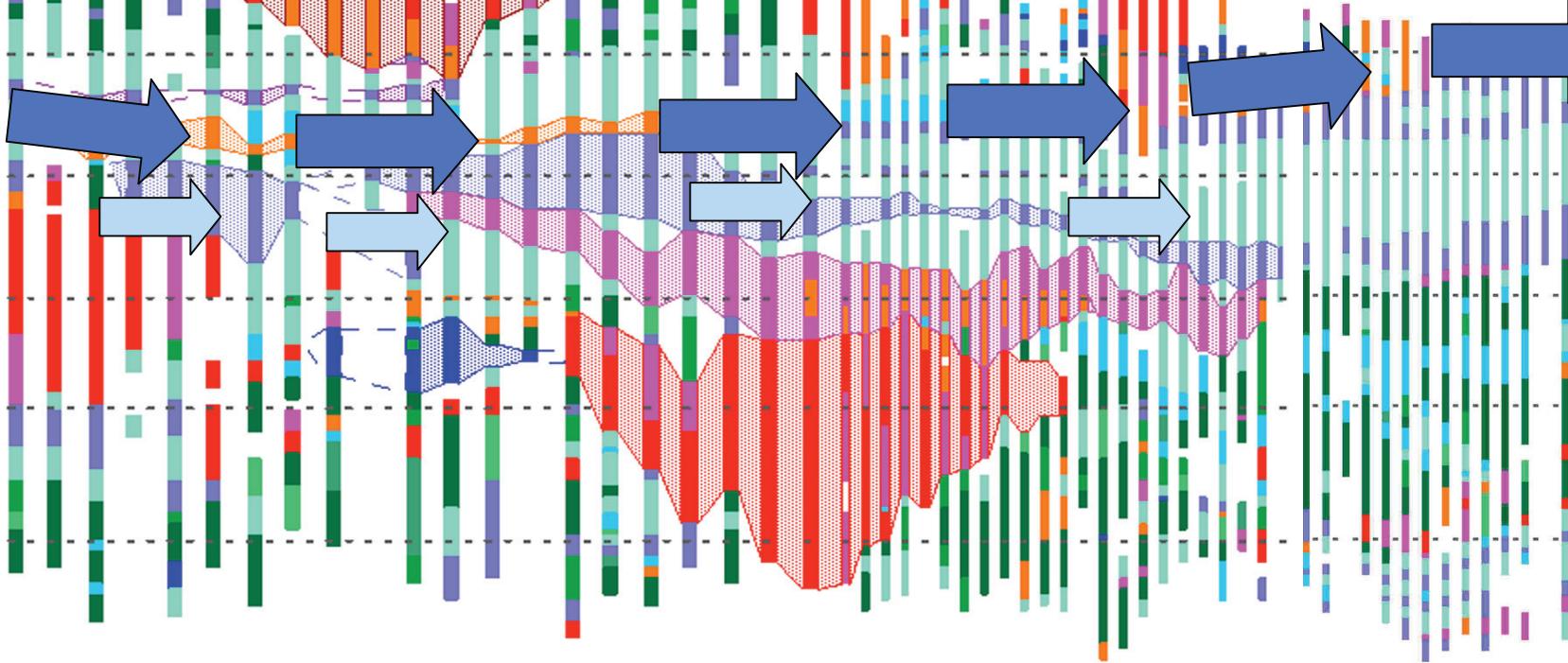
5

10

15

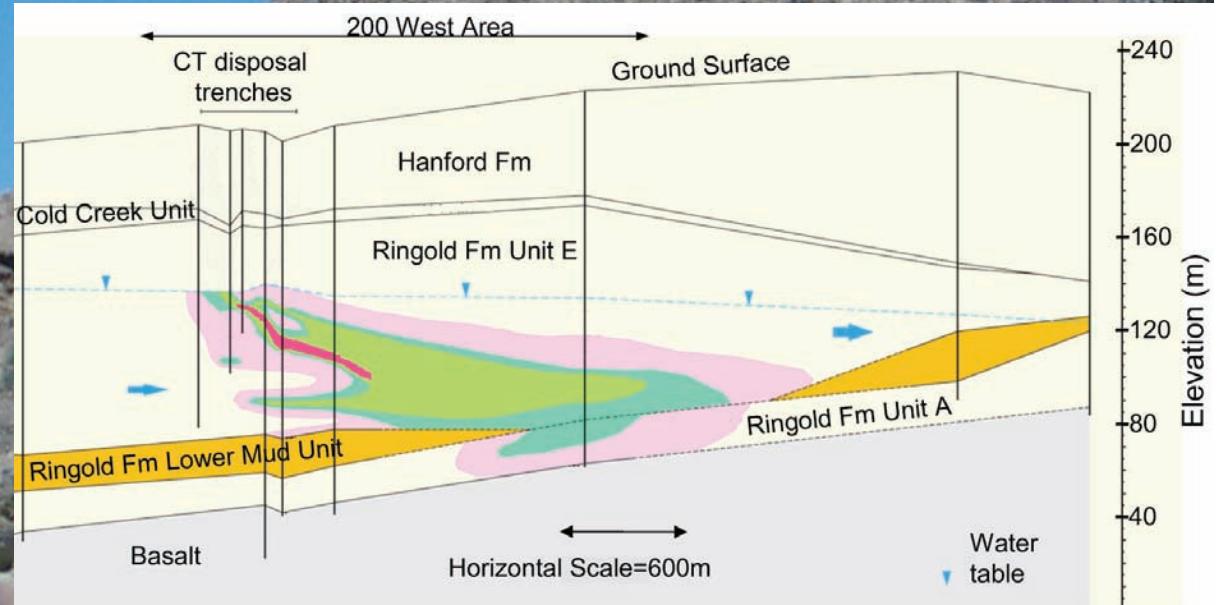
20

**Northing (m)**

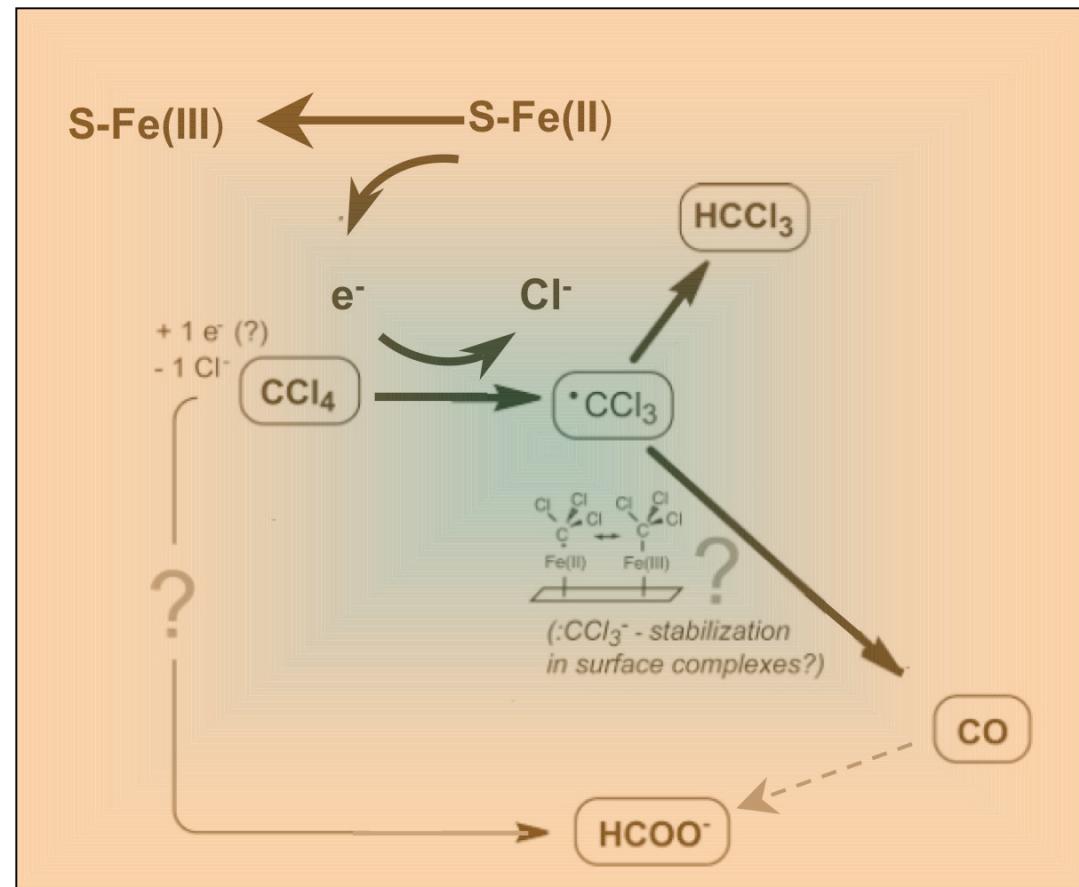
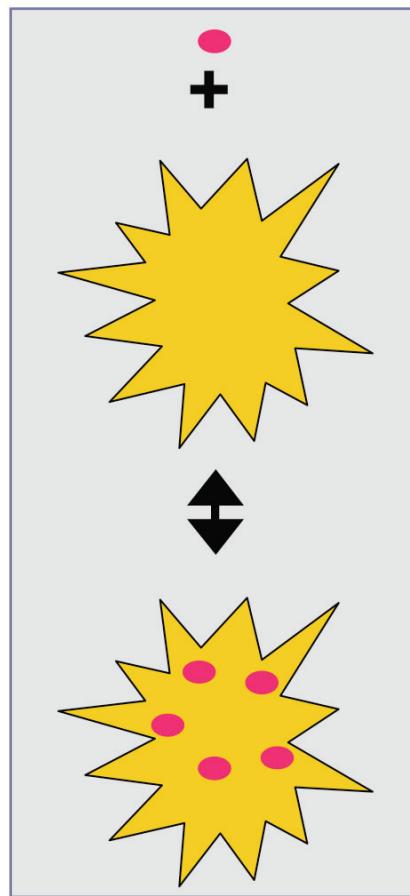


# Hanford plume

- Geologically old sediments with significant diagenesis
- CT Plume ~ 0.5 km<sup>3</sup> & transport distances of kms



# More complex reactions – redox and pH sensitive



# Conclusions

Plume transport dynamics can be controlled by geochemistry

Extremely small proportion of the total aquifer comprising very small particles can control on transport.

Spatial information and underlying geochemical (and physical) sedimentary aquifer properties can be obtained through lithofacies mapping and correlation

# Questions - aquifer property heterogeneity & reactive transport

- What are the biogeochemically reactive sites?
- What is the relationship of the reactivity and permeability?
- At what spatial scales must we define the aquifer reactivity and permeability in order to predict reactive transport?

# Acknowledgements

## Collaborators

- ❑ Rabideau, UB
- ❑ Knight & Moysey,  
Stanford
- ❑ Ritzi & Domenic, Wright  
State U
- ❑ Weissmann, UNM
- ❑ Murray & Scheibe,  
PNNL

## Students and Postdocs

- ❑ Polmanteer, Lilienthal,  
Wang, McGrane
- ❑ Divine, Taylor & many  
undergrad researchers

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- ❑ NSF, Hydrologic  
Sciences
- ❑ DOE-This program!



Enviro geosciences faculty

# Is micro-scale chemical heterogeneity important to R prediction?

- What is the sorbent causing contaminant retardation?
- Where is the sorbent?
- What are the characteristics of sorbent interactions with PCE?

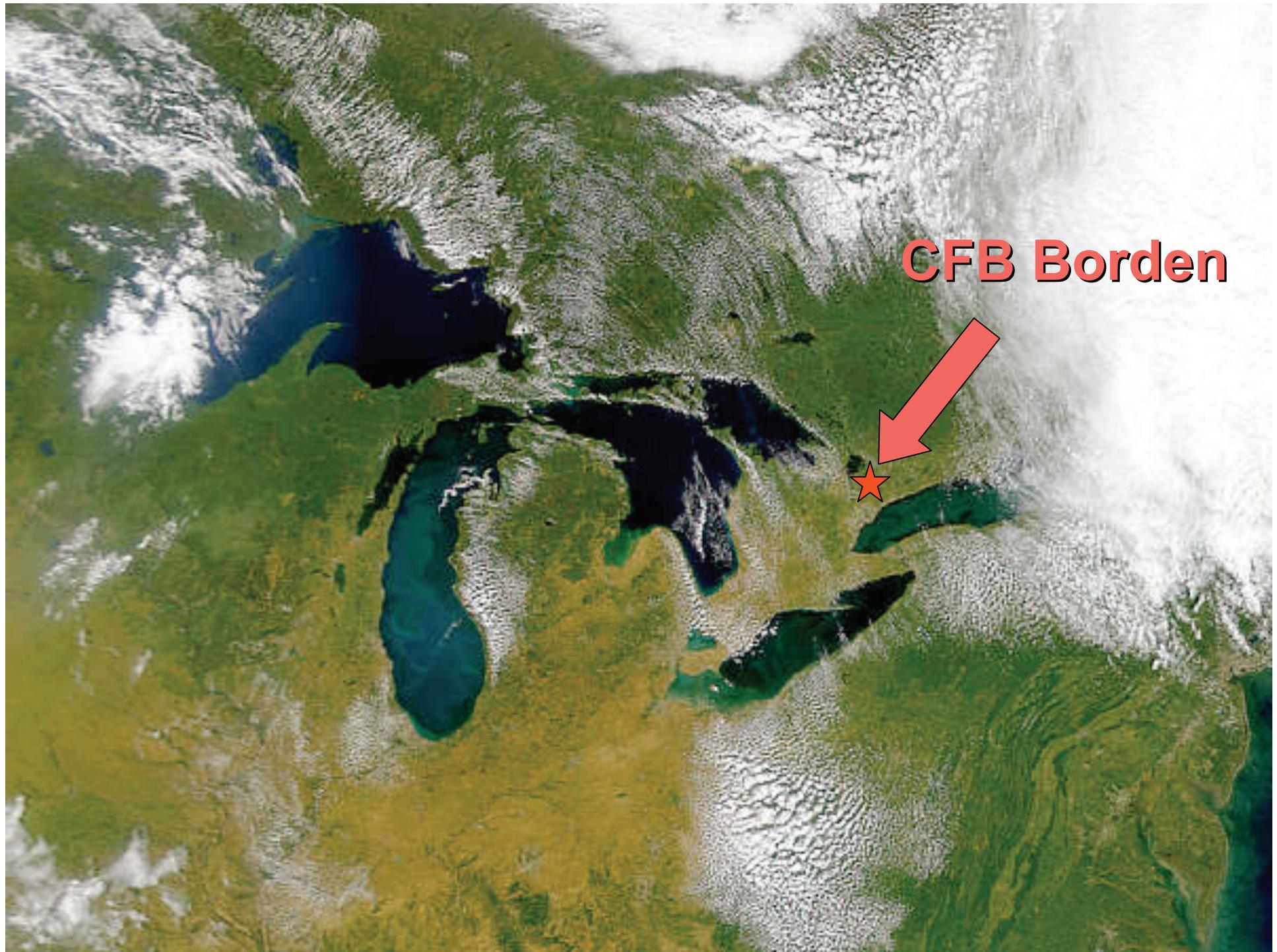
# Groundwater contaminant transport

- Predictions (models) used to:
  - To estimate long term societal/ecological impacts
  - Assign risk to prioritize remediation needs
  - Plan efficient remedial design

*Understanding and incorporating heterogeneous distributions of subsurface properties authentically will allow us to do all of these better!*

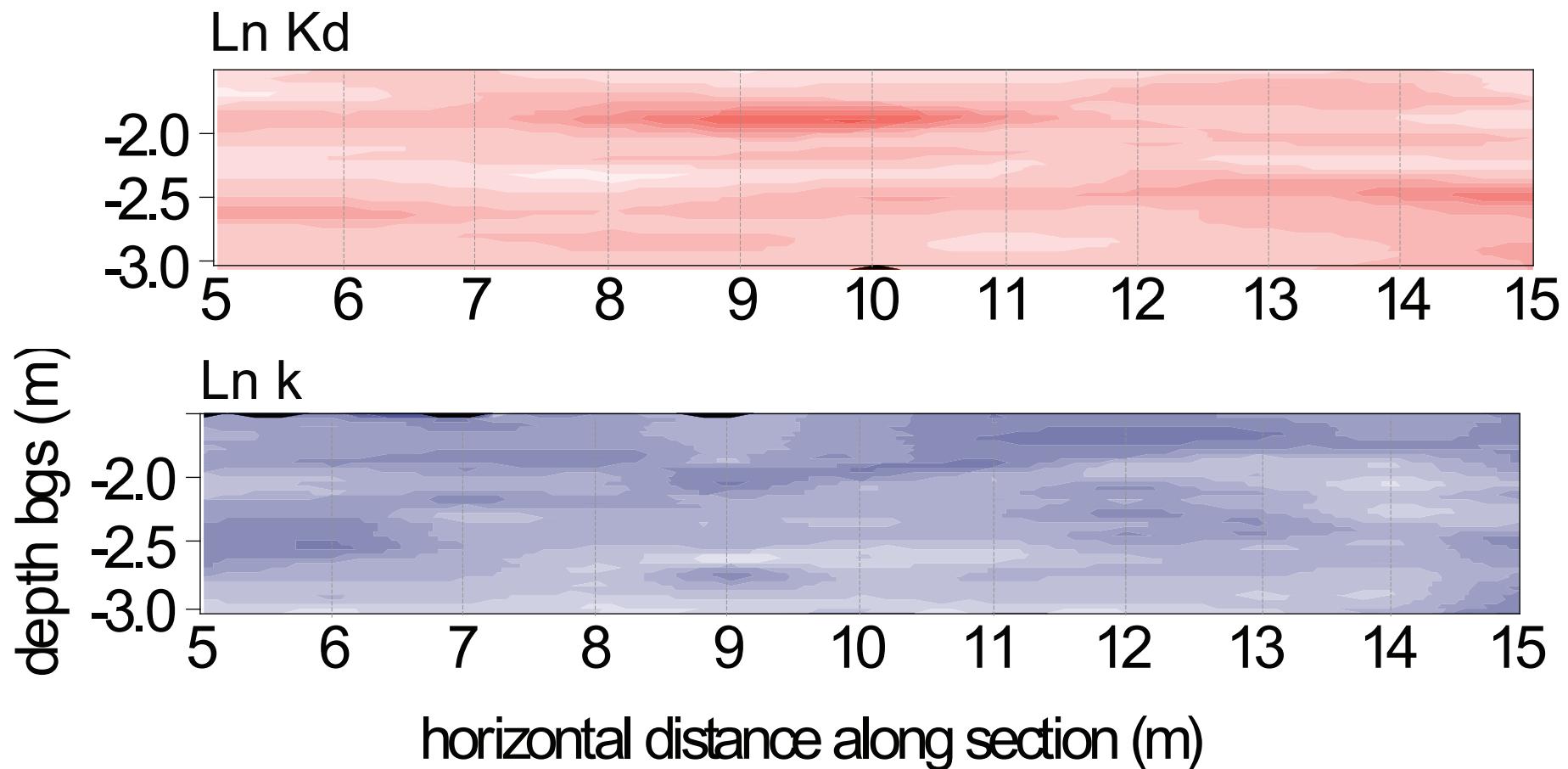
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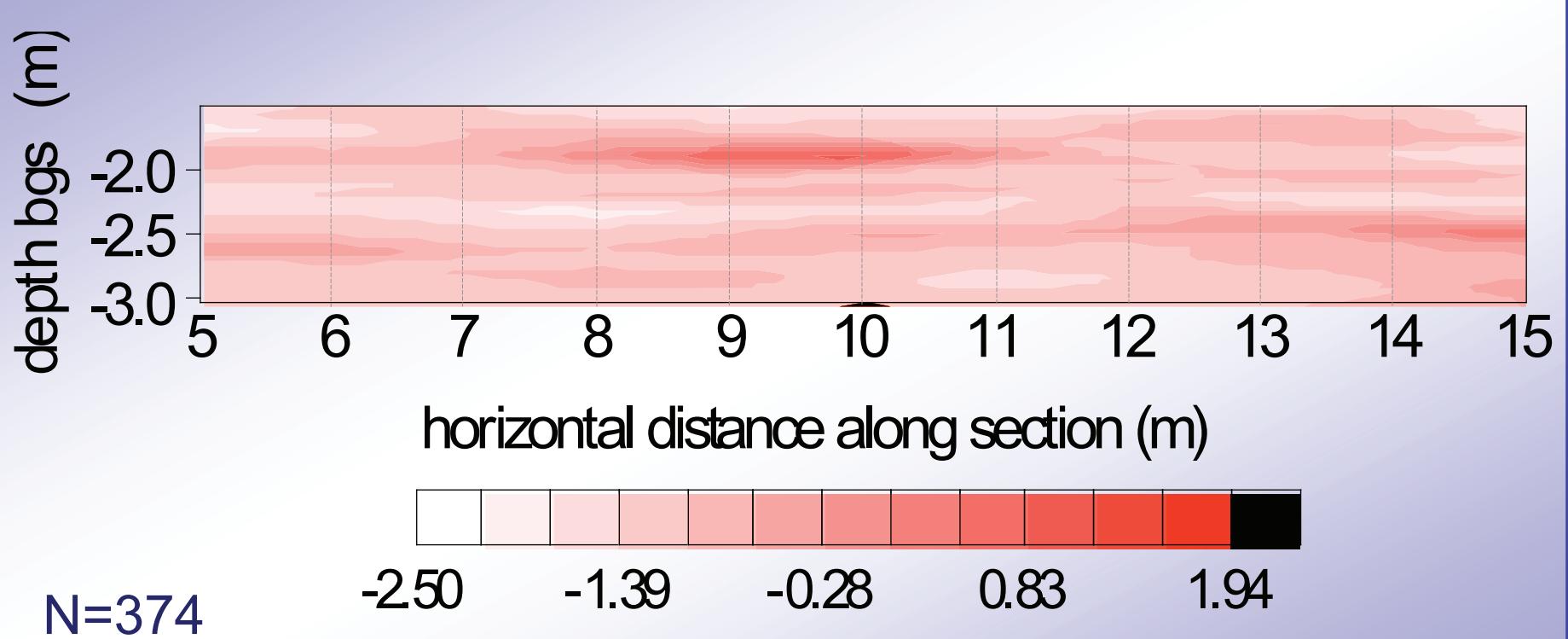


**CFB Borden**

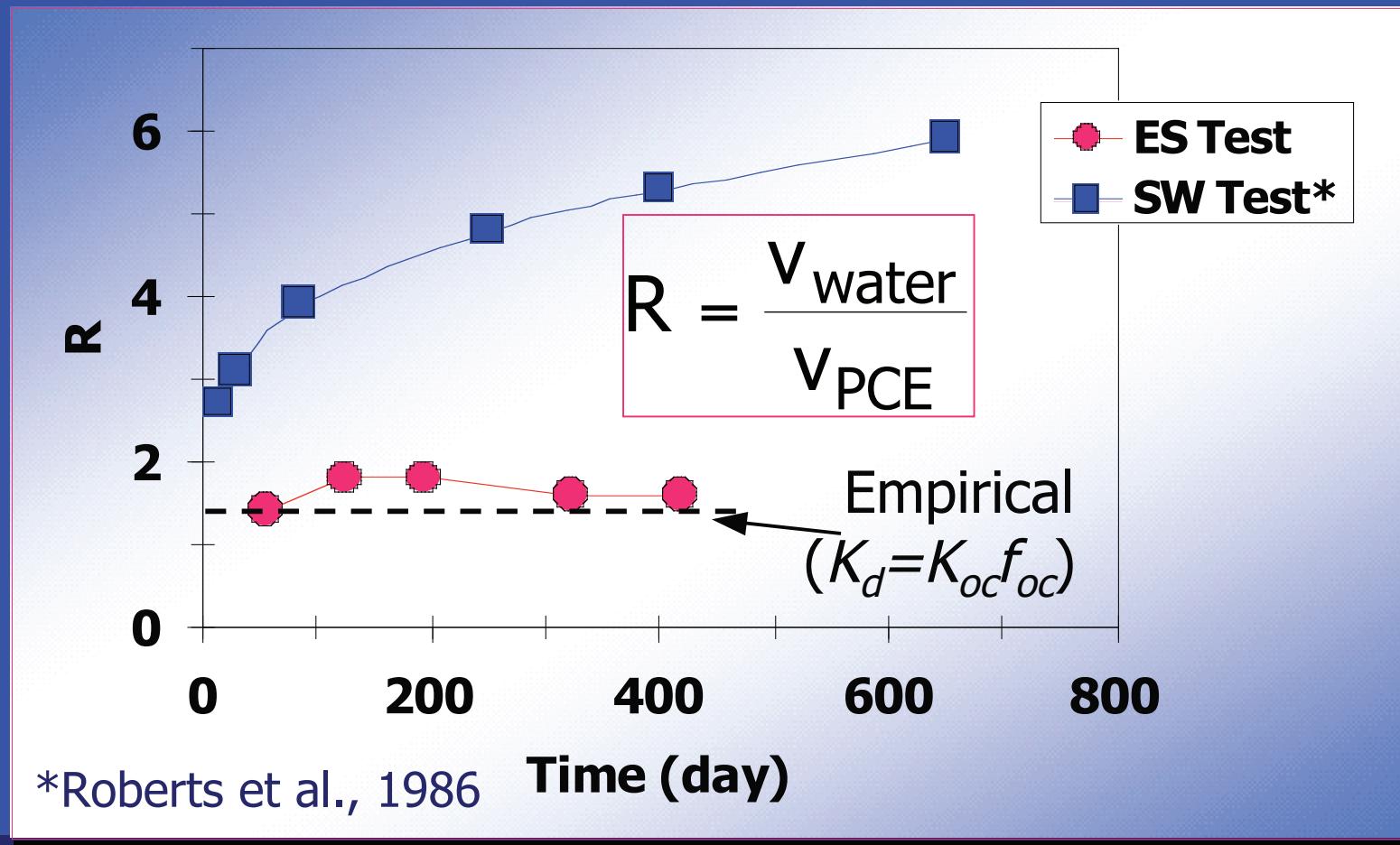
# Comparison between distributions – same variance!



# Spatial distribution of ln (Kd)



# ES plume demonstrates “ideal” retardation

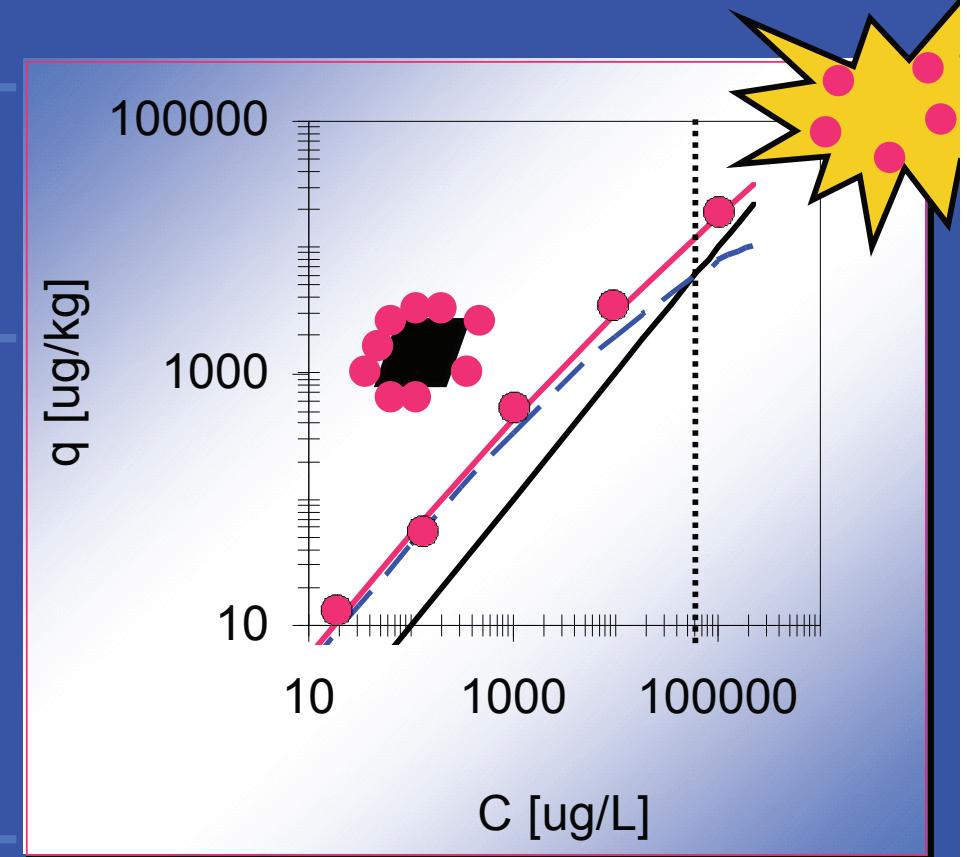


# Competitive sorption can result in transport trends

Observed Predicted

ES 1.4-2.0 1.7-2.6

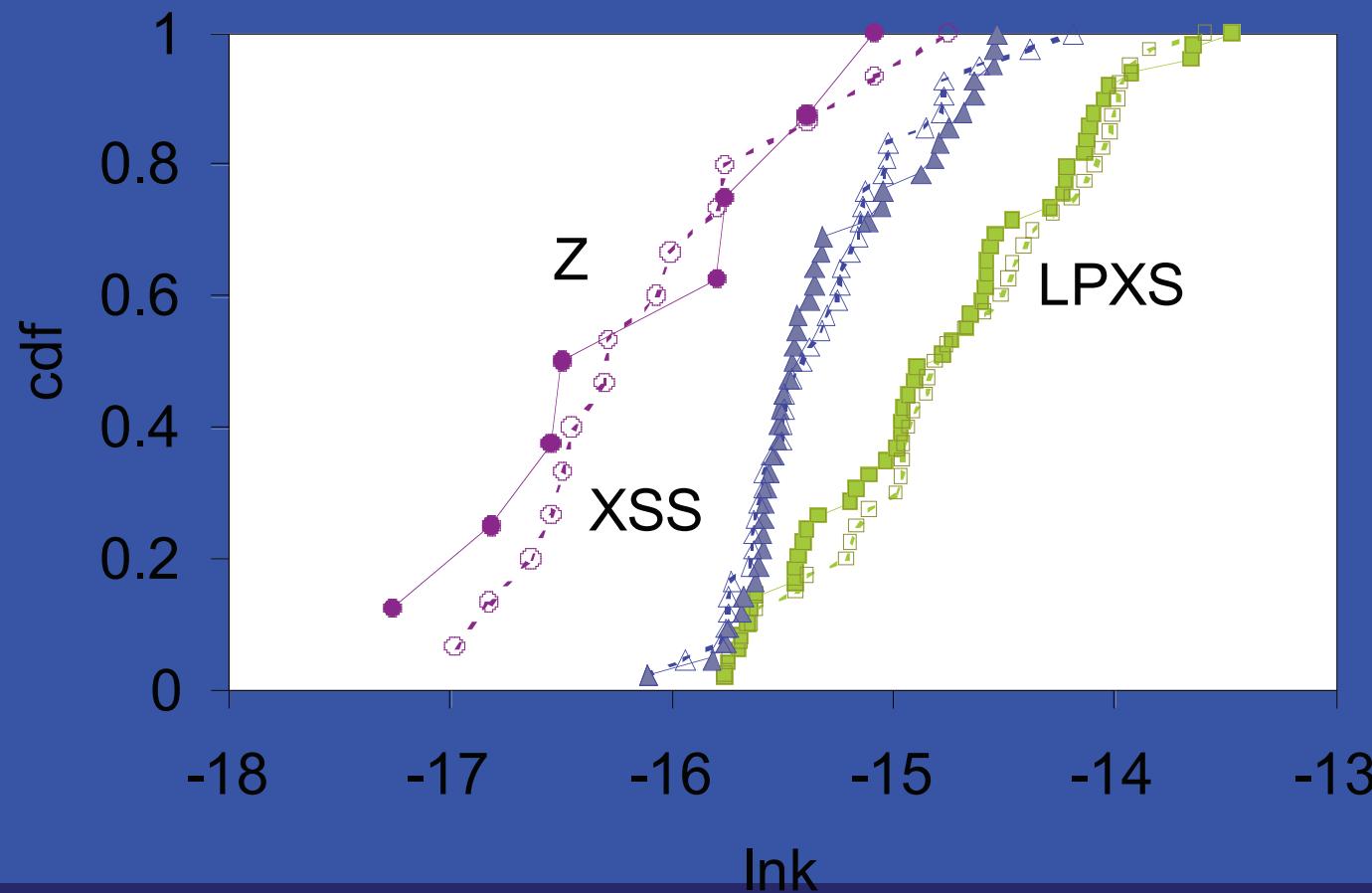
SW 2.7-5.9 ~3.8-6.3



# Summary from our plume saga...

- Different R (and trending R in SW) behavior is consistent with our hypotheses about:
  - the grain-scale geochemical properties of the sorbent &
  - interactions with contaminants
- Enhanced dispersion in SW test is consistent with the plume-scale distribution of sediment geochemical properties

# Lithofacies predict k well in most cases



# Comparisons between two mapped directions

- Permeability well predicted for 7 of 9 lithofacies
- Poor predictions for two facies
  - (sorting implicated, ongoing work)
- Lithofacies distribution is also well predicted
  - fraction of occurrences
  - average thickness

# Borden & Hanford ‘bookends’

|                                     | Borden                                    | Hanford                                      |
|-------------------------------------|---|--|
| CT                                  | Retarded,<br>not transformed              | ??   |
| Sediments                           | Young,<br>little diagenesis               | Old (Pliocene),<br>significant<br>diagenesis |
| Plume size &<br>transport distances | ~20 – 400 m <sup>3</sup><br>10s of meters | ~0.5 km <sup>3</sup><br>10s of kms           |

# Highlight some insights

- And some outstanding questions
- Questions – at what scale(s) and for what problems do rate limited reactions at the grain scale limit overall mass flux (source/sink)
- Flux concept (not just concentration)
- What features (physical, lithologic) and at what resolution (particularly in the vertical) do (various) geophysical techniques resolve lithology, what hydrogeologic property insights are gained from geophysical work
- Stochastic versus deterministic (type) approaches and scale of transport
- What scale of geochemical and physical heterogeneityies combined affect (control) reactive solute transport (or have significant affects on)
- very fine particles and/or a very tiny proportion of the aquifer material can exert an impact on overall plume transport
- What is the relationship between  $k$  and  $K_d$

# notes

- Add flow arrows to cross section
- Wrap up word slide provides summary of importance of sed architecture on hydrogeologic picture
- What about geophysics – well, what do the GPR images actually show us? What information at what spatial scales does geophysics provide? (a vignette here)
- Important for small scale field efforts that, in many ways mimic scale of importance for contaminant transport
- Aside notes – important themes on what scale of geologic features (heterogeneity) impact transport across an entire plume? (maybe quite small), what proportions and so on...